

High-resolution energy-selected study of the reaction $\text{NH}_3^+ @ \text{NH}_2^+ + \text{H}$: Accurate thermochemistry for the $\text{NH}_2/\text{NH}_2^+$ and $\text{NH}_3/\text{NH}_3^+$ system

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INTRODUCTION

As the simplest amine, NH_3 and its cation NH_3^+ are of fundamental interest to both chemistry and biology. Since this simple system is amenable to accurate theoretical calculation, reliable 0 K bond dissociation energies (D_0) obtained for this system would provide a challenge and thus the further development of the next generation of computational schemes. Based on energy conservation, the D_0 values for $\text{NH}_2\text{-H}$ and $\text{NH}_2^+\text{-H}$ can be determined by measurements of the ionization energies (IEs) for NH_2 and NH_3 and the appearance energy (AE) of NH_2^+ from NH_3 (see Fig. 1).

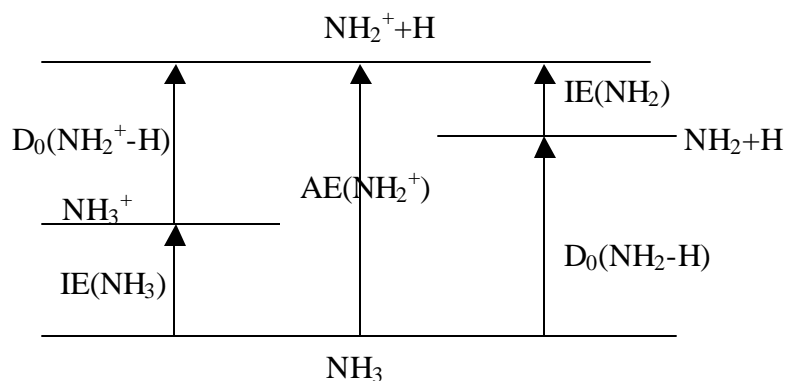


Figure 1. Schematic diagram showing the relation of $\text{IE}(\text{NH}_2)$, $\text{IE}(\text{NH}_3)$, $\text{AE}(\text{NH}_2^+)$, $D_0(\text{NH}_2\text{-H})$, and $D_0(\text{NH}_2^+\text{-H})$.

The most general and reliable method for AE measurements involves the use of the photoelectron-photoion coincidence (PEPICO) technique. The conventional PEPICO scheme based on threshold photoelectron (TPE) detection has been widely employed for dissociation studies of state- or energy-selected ions. However, the error limits of AE measurements achieved in such measurements have been limited by the relatively low resolution and hot electron tail associated with the TPE transmission function. We have demonstrated recently that the PFI-PE method is free from the hot-tail problem and thus AE values for a range of molecules can be determined with unprecedented precision by using the PFI-PEPICO technique.¹

The $\text{IE}(\text{NH}_3)$ and $D_0(\text{NH}_2\text{-H})$ have been accurately determined previously. We have performed a PFI-PEPICO study of NH_3 near its 0 K dissociation threshold or AE for NH_2^+ . This measurement along with the known $\text{IE}(\text{NH}_3)$ and $D_0(\text{NH}_2\text{-H})$ has allowed the determination of highly accurate values for $D_0(\text{NH}_2^+\text{-H})$ and $\text{IE}(\text{NH}_2)$.

EXPERIMENT

The present experiment was performed using the multipurpose photoelectron-photoion apparatus of the Chemical Dynamics Beamline (9.0.2) at the Advanced Light Source. The light timing structure consisted of 272 bunches followed by a dark gap of 112 ns. A 2400 lines/mm grating (dispersion = 0.64 Å/mm) was used to disperse the first order harmonic of the undulator VUV beam with entrance/exit slits set at 30/30 $\mu\text{m}/\mu\text{m}$. The resulting monochromatic VUV beam was then focused into the photoionization/photoexcitation (PI/PEX) center of the photoelectron-

photoion apparatus. The procedures for PFI-PEPICO measurements have been described in detail previously.¹ The PFI-PE selection was achieved by employing the electron TOF scheme. A dc field of 0.2 V/cm was maintained at the PI/PEX region to sweep background electrons formed by direct and prompt autoionization toward the electron detector prior to the application of the electric field pulse for Stark ionization. The PFI pulse (height = 7.3 V/cm, width = 200 ns) was applied ≈ 10 ns after the start of the dark gap. NH_3 sample was introduced into PI/PEX region as a skimmed neat NH_3 supersonic beam (stagnation pressure = 600 Torr at room temperature). Coincidence spectra were recorded using a multi-channel scaler triggered by the detection of PFI electron.

RESULTS AND DISCUSSION

A. Breakdown curves for NH_2^+ and NH_3^+

A series of PFI-PEPICO TOF spectra for NH_2^+ and NH_3^+ were recorded near the $\text{AE}(\text{NH}_2^+)$, in the range of 15.65–15.85 eV. When photon energies are far below $\text{AE}(\text{NH}_2^+)$ (ND_2^+), only parent ion was observed. With the increase of photon energy, relative intensity for the NH_2^+ daughter ion increased correspondingly. At photon energies beyond the 0 K dissociation threshold, the NH_3^+ parent ion intensity was found to remain constant at 10% for NH_3^+ . This residual of parent ion signal was attributed to false coincidences associated with the dissociative photoionization of NH_3 dimers and clusters formed in the supersonic beam.

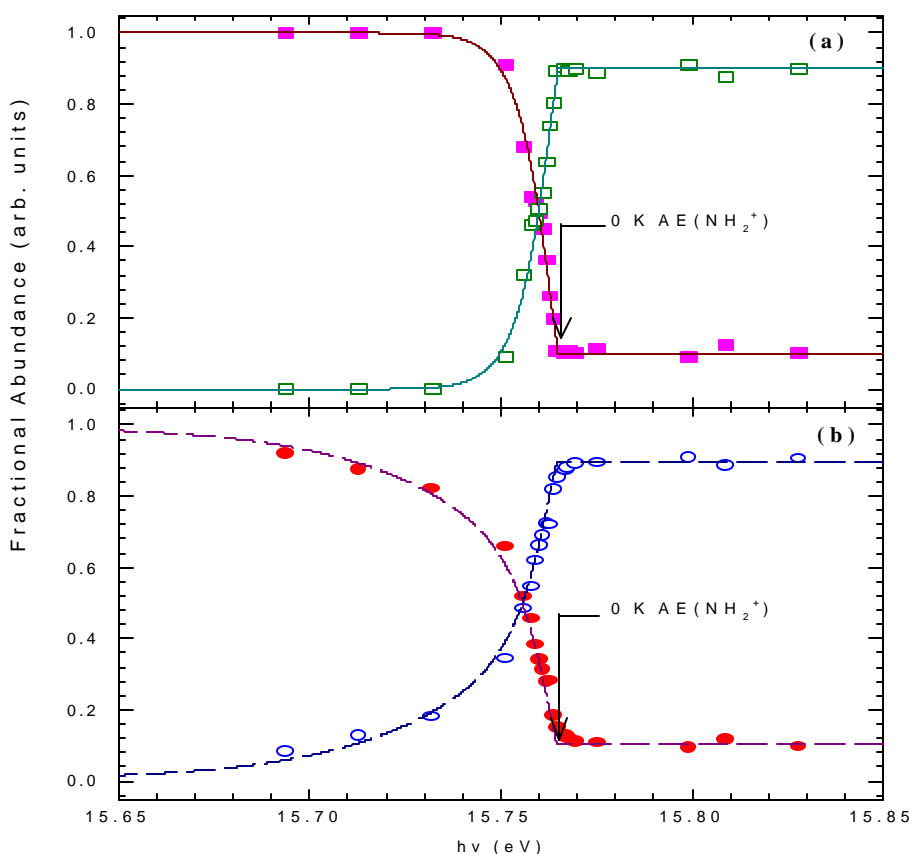


Figure 2 (a) Breakdown curves for NH_2^+ (\square) and NH_3^+ (\blacksquare) in the $h\nu$ range of 15.69–15.83 eV obtained using only the cold NH_2^+ and NH_3^+ ion signals. The solid lines (—) are simulated curves obtained assuming a cold NH_3 sample at 60 K. (b) Breakdown curves for NH_2^+ (\circ) and NH_3^+ (\bullet) in the $h\nu$ range of 15.69–15.83 eV obtained using the entire (thermal and cold) NH_3^+ and NH_2^+ ion signals. The dashed (—) curves are simulation calculated assuming 10% thermal (298 K) and 90% cold (60 K) NH_3 sample.

After background corrections, each TOF peak was simulated using two Gaussian functions with widths of 100ns and 300ns for the cold and thermal component respectively. This analysis results in breakdown curves for NH_3^+ and NH_2^+ for the cold [Fig. 2(a)] and thermal [Fig. 2(b)] NH_3 samples. Although the fractional abundance for the parent (daughter) ion does not go to zero (unity) at the AE in this case, the 0 K AE(NH_2^+) is distinctly identified by the sharp break at 15.765 ± 0.001 eV [marked as 0 K AE(NH_2^+) in Figs. 2(a) and 2(b)] of the breakdown curves, at which the fractional abundance for the parent (daughter) reaches its lowest (highest) value. We emphasize that the 0 K AE(NH_2^+) determined here by the sharp break is unambiguous and does not depend on a detailed simulation of the breakdown curves.

The breakdown diagram was simulated using procedures described in previous studies. The respective solid and dashed lines in Figs. 2(a) and 2(b) were obtained by convoluting the thermal energy distribution for NH_3 with a step function at the 0 K AE(NH_2^+), confirming the value of 15.765 ± 0.001 eV for the 0 K AE(NH_2^+) from NH_3 . Due to rotational cooling of NH_3 in molecular beam, the cold breakdown curves of Fig. 2(a) are sharper than those of Fig. 2(b). By assuming a temperature of 60 K for NH_3 in the molecular beam, we have obtained an excellent fit (solid lines) of the cold breakdown curves shown in Fig. 2(a). The dashed lines in Fig. 2(b) are calculated breakdown curves assuming the NH_3 sample consisting of $\approx 10\%$ thermal (298 K) background and $\approx 90\%$ cold (60 K) beam sample. The simulation of the breakdown curves also assumes a constant false coincidence background of 10% at $h\nu$ values above the AE.

B. Thermochemistry for the $\text{NH}_3^+/\text{NH}_2^+$ system

Table I compares the AE(NH_2^+) values obtained in the present experiment with literature values. The values in bold fonts are the best experimental values recommended in the present study. These highly accurate energetic data has stimulated a state-of-the-art *ab initio* quantum chemical calculation by Dixon *et al.*³

Table I. Comparison of values for 0 K heats of formation ($\Delta H^\circ_{\text{f0}}$) for NH_2 , NH_2^+ , NH_3 , and NH_3^+ and 0K AE for NH_2^+

AE (eV)	IE (eV)		$\Delta H^\circ_{\text{f0}}$ (kcal/mole)			
NH_2^+	NH_3	NH_2	NH_3	NH_3^+	NH_2	NH_2^+
15.765 ± 0.001	10.1864 ± 0.0001	11.1633 ± 0.0025	-9.31 ± 0.08	225.59 ± 0.08	45.17 ± 0.09	302.60 ± 0.08
ab initio predictions (Ref. 3)						
15.77	10.171	11.176	-9.1	225.4	45.3	303.0

References

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